CHEMICAL AND ISOTOPIC
GROUND-WATER EVALUATION
PONCE WASTE FACILITY
PONCE, PUERTO RICO

Submitted to

LAW ENGINEERING TESTING COMPANY

MARIETTA, GEORGIA

by

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1.0 INTRODUCTION

1.1 Purpose and Objectives

The purpose of this report is to review and analyze geochemical and isotopic ground-water data from the Ponce Waste Site and, based on these data and existing geologic and potentiometric data, to evaluate the ground-water flow regime in the Juana Diaz Formation on the site. Specific objectives are:

1) estimate mean ground-water residence times ("ages") of Juana Diaz Formation waters using radiocarbon methods. Mean subsurface residence times often provide valuable insight into the flow patterns of ground-water systems, in that ground-water ages are the mean time elapsed since the sampled ground water was in contact with the surface or near-surface environment.
2) evaluate the origin of ground water in the Juana Diaz Formation and potential ground-water flow and mixing patterns based on chemical and isotopic data from ground and surface waters.
3) review existing geologic and potentiometric data and develop a conceptual model of the ground-water flow regime in the Juana Diaz Formation on the site.

1.2 Data Sources

This report is based solely on verbal and written information provided by Law Engineering Testing Company and Geochron Laboratories of Krueger Enterprises, Incorporated. The following information was used:

Law Engineering:

- Dr. James Wallace, personal communication.
- Mr. James Gustin, personal communication.
- Ponce Waste Facility, Ponce Puerto Rico, Site Characterization Report, July 22, 1983.
- Ponce Waste Facility, Hydrogeologic Assessment/Monitoring Well Installation Draft Report, October 27, 1983.
- Ponce Waste Facility, Hydrogeologic Assessment/Phase II Monitoring Well Installation, incomplete review draft, March 19, 1984.
- Analytical Results (chemical) from RECRA Environmental Laboratories, dated March 7, 1984 (January 12, 1984 sampling) and dated March 7, 1984 (November 17 and 21, 1983 samplings).

Geochron Laboratories:

- Harold Krueger, personal communication.
- δD and $\delta^{18}O$ analytical results.
- ^{14}C and ^{13}C analytical results.

2.0 CHEMICAL ANALYSES

Chemical analyses of ground-water samples from 4 onsite and 4 offsite wells were reviewed. Many of the wells had analyses from several sampling dates. Water analyses listed in Table 1 are believed to be representative of the ground-water regimes sampled. Some of the data included are HCO_3^- estimates (see section 5.0). Five analyses are from the Juana Diaz Formation (MW-2, 3, 4, and Offsite #1) and three analyses are from the Ponce Formation (Offsite #2, 3, and 4). MW samples were collected from onsite monitoring wells whose locations are shown on Figure 1. The offsite wells are located within a 5 mile radius of the site (Gustin, 1984).

2.1 Stiff and Trilinear Diagrams

Results of major ion analyses have been plotted on Stiff (1951) diagrams, Figure 2, and on a trilinear diagram, Figure 3, in the manner of Piper (1944). Stiff diagrams facilitate the comparison of total solute concentration and ionic composition by the utiliztion of graphical shapes. The shape of the diagram represents composition, while the size reflects concentration. The triliear diagrams show the percent contribution of major ions making up the total solute concentration, independent of actual ionic strength (salinity) of the water.

Two distinct water types are evident from the Stiff and trilinear plots. Juana Diaz Formation waters have very high solute concentrations (mean concentration meq l^{-1}) and are of the sodium-magnesium-chloride-sulfate type. Ponce Formation waters have considerably lower solute concentrations (mean concentration 49 meq l^{-1}) and are of the no dominant cation-anion type. The contribution of ions from specific aquifer minerals and

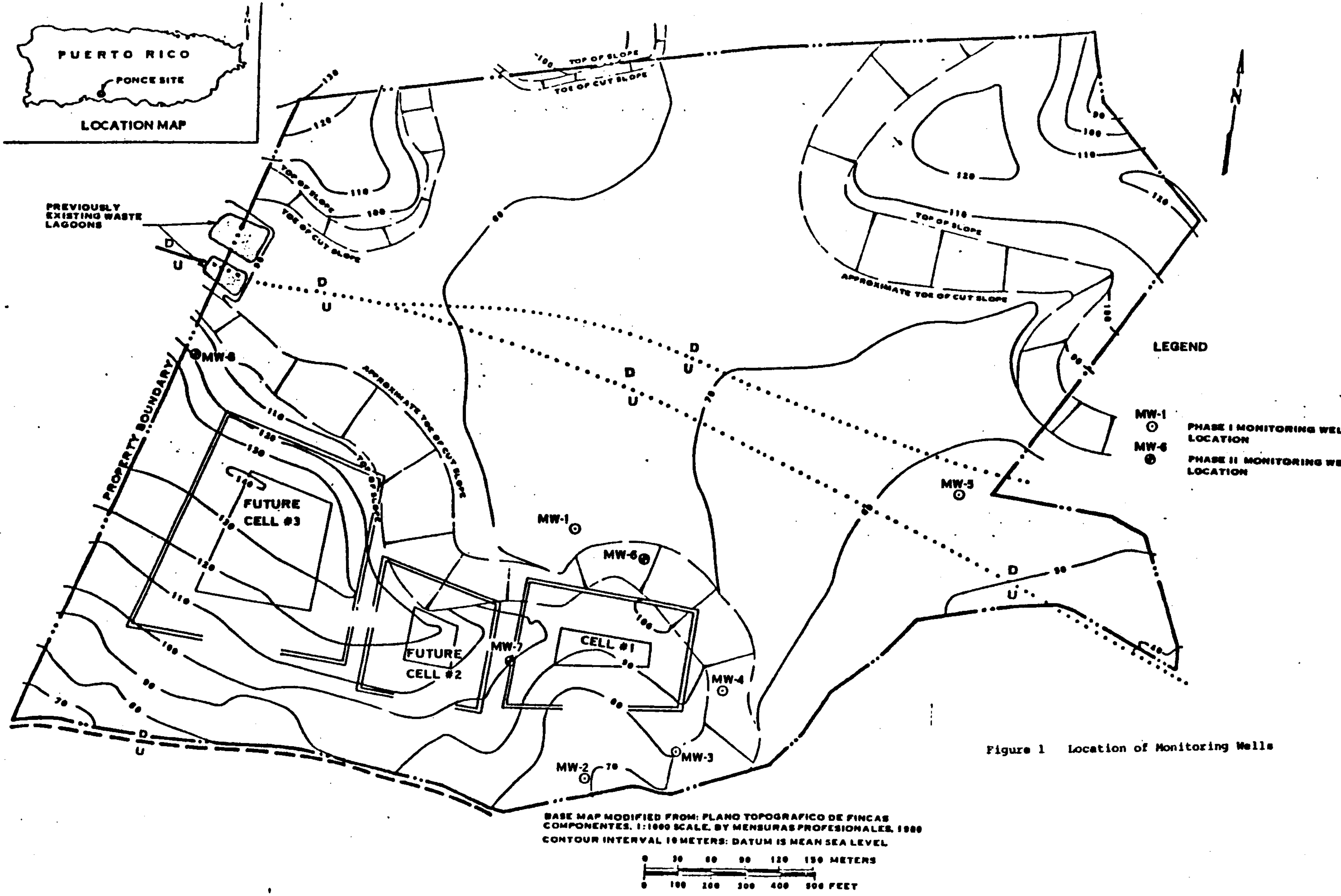
Table 1 Summary of Chemical Analyses

				Concentration meq l^{-1}							
Sample	Formation	Temp °C	pH[1]	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}	Cl^-	Remarks
MW-2	Juana Diaz	24.4	6.7	44.8	0.4	22.6	19.3	4	32.1	51.9	HCO_3^- est
MW-3	Juana Diaz	25.0	6.6	65.7	1.6	39.8	60.9	9	48.9	113.7	HCO_3^- est
MW-4	Juana Diaz	25.0	6.5	45.7	1.6	48.5	43.6	9	32.5	102.1	HCO_3 est
MW-7	Juana Diaz	25.6	6.8	27.8	1.0	3.4	14.0	4	20.2	25.2	HCO_3^- est
OF-1	Juana Diaz	27	7.6	59.6	-	15.0	24.0	9.2	31.4	57.8	
OF-2	Ponce	27	7.7	16.4	-	10.3	4.5	5.8	5.7	19.3	
OF-3	Ponce	27	7.4	8.9	-	9.8	4.9	5.7	3.9	13.9	
OF-4	Ponce	26	8.0	10.4	-	5.0	3.2	6.7	7.2	4.5	

OF are offsite wells, see text.

[1] pH values of Juana Diaz may be laboratory.

Sampling dates of OF data are unknown; MW sampling dates are 1/12/84.


N
PUERTO RICO
PONCE SITE
LOCATION MAP
PREVIOUSLY EXISTING WASTE LAGOONS
PROPERTY BOUNDARY
TOP OF SLOPE
TOE OF CUT SLOPE
APPROXIMATE TOE OF CUT SLOPE
FUTURE CELL #3
FUTURE CELL #2
CELL #1
MW-1
MW-2
MW-3
MW-4
MW-5
MW-6
MW-7
MW-8
D
U
70
80
90
100
110
120
130
140
LEGEND
MW-1 PHASE I MONITORING WEL LOCATION
MW-6 PHASE II MONITORING WE LOCATION
0 30 60 90 120 150 METERS
0 100 200 300 400 500 FEET

BASE MAP MODIFIED FROM: PLANO TOPOGRAFICO DE FINCAS COMPONENTES, 1:1000 SCALE, BY MENSURAS PROFESIONALES, 1980
CONTOUR INTERVAL 10 METERS: DATUM IS MEAN SEA LEVEL

Figure 1 Location of Monitoring Wells

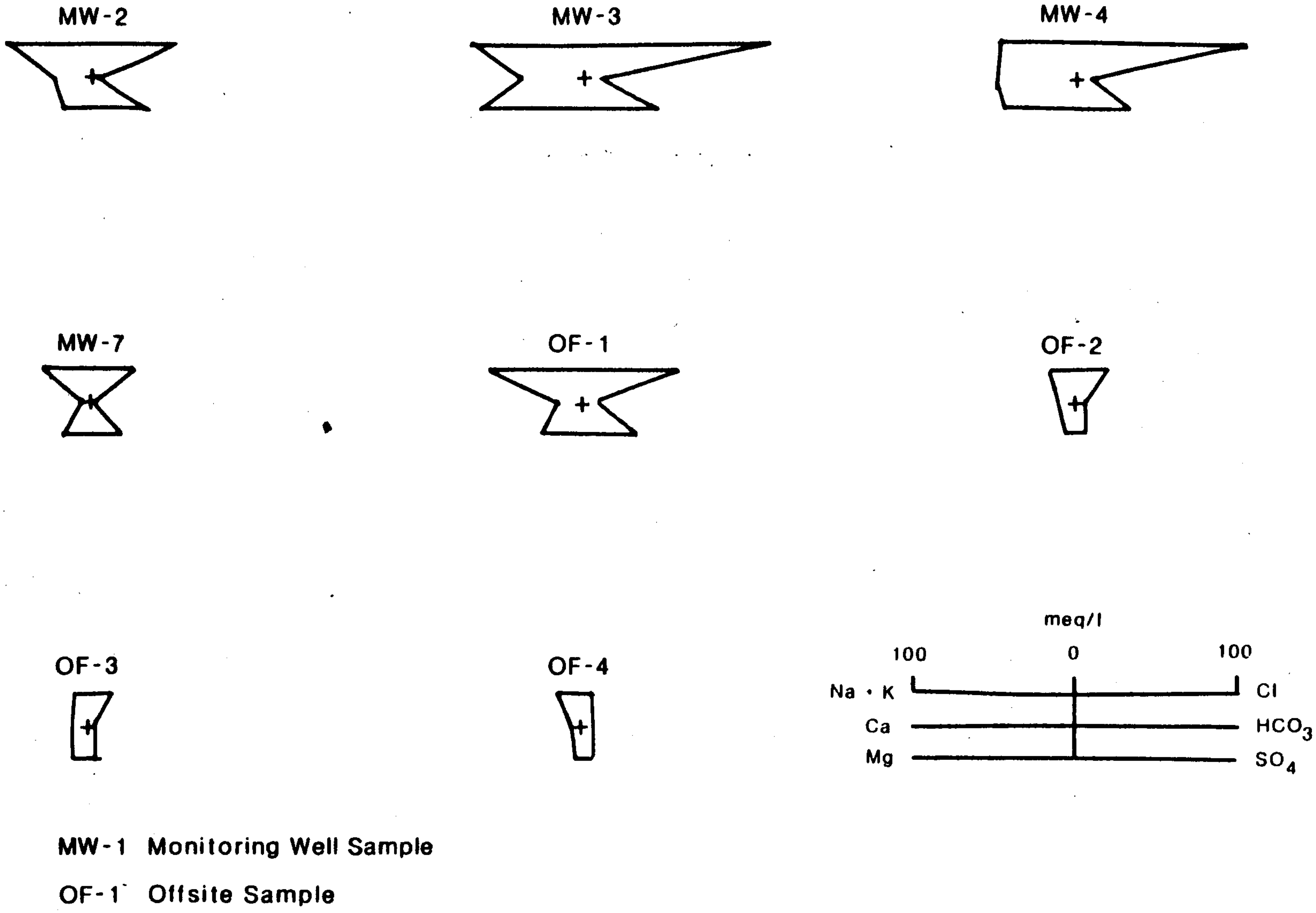


Figure 2 Stiff Diagrams

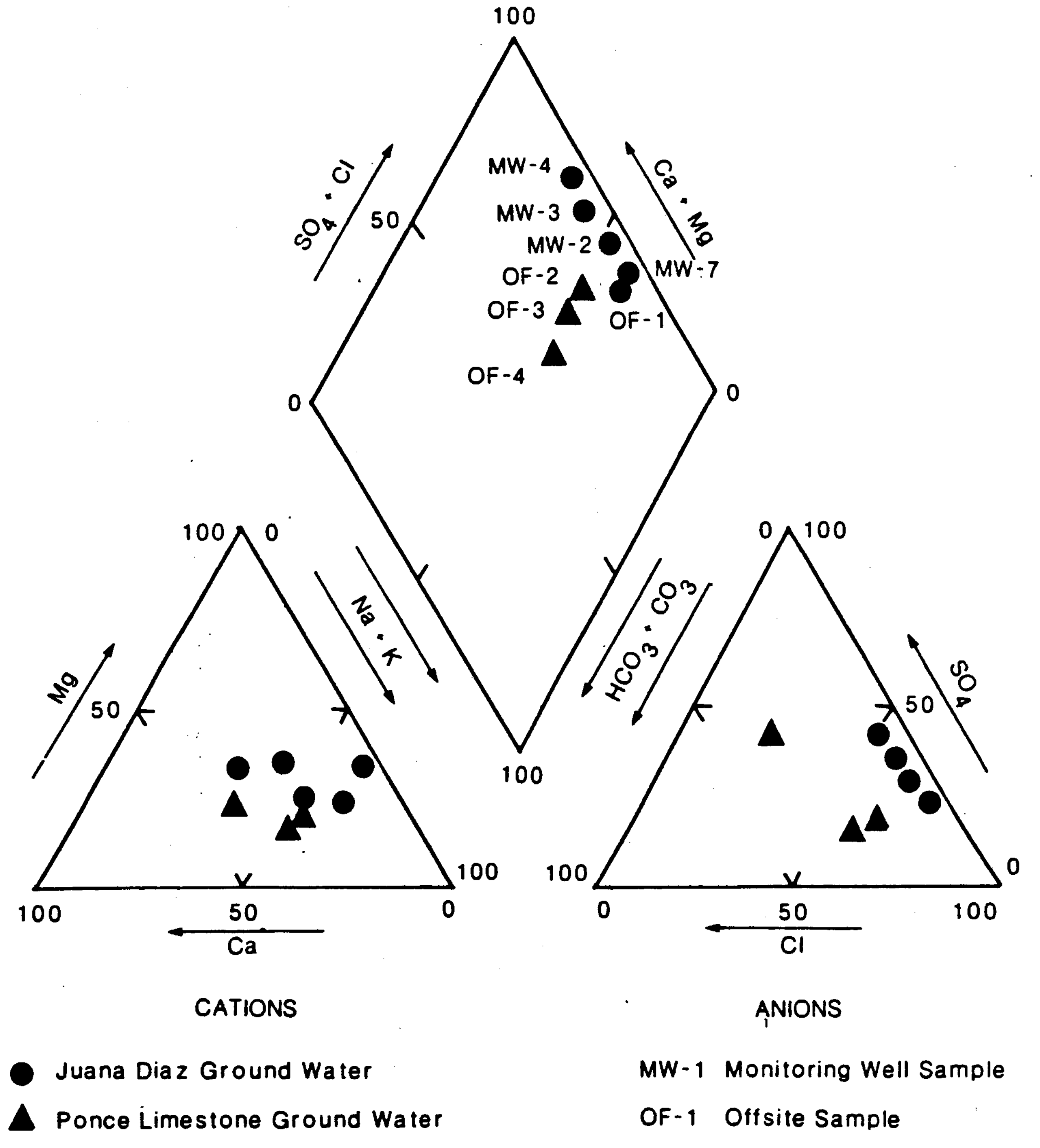


Figure 3 Trilinear Diagram. Charges have been omitted from ionic species.

connate water sources cannot be determined from these plots. Rock-water chemical equilibrium analysis, which calculates the saturation indices (SI) of a water, could provide valuable insight into ion sources and observed variations of solute concentrations in Juana Diaz Formation waters. (Saturation index is a measure of the thermodynamic tendency of a water to dissolve or precipitate a mineral species.) Such calculations require reliable field pH, temperature, and HCO_3^- measurements. Field HCO_3^- measurements are not available with the data sets. Saturation indices would also be useful in the evaluation of ionic exchange processes and water chemistry evolution along flow paths.

Nonetheless, some pertinent observations may be made from the major ion data:

1) Juana Diaz Formation waters are similar to other ground waters from silty, clayey, shaly aquifers of marine origin. Such fine grained sediments often contain absorbed ions on clay minerals from original saline solutions. These ions are not completely removed by ground-water flushing because of low hydraulic conductivities of the rocks. Such low hydraulic conductivities are found in the Juana Diaz Formation. The high solute concentrations of Juana Diaz Formation waters are not typical of carbonate aquifers or other fast flushing aquifer systems. Observed solute concentrations are considerably less than those found in brines and aquifers principally containing connate waters of marine origin.
2) The large variation in solute concentrations (95.6 to 339.6 meq l^{-1}) of the Juan Diaz Formation waters may be indicative of mineralogical variations of water-bearing horizons. A correlation cannot

APPENDIX

A - FIELD PROCEDURES

TABLE 5 ESTIMATED DRILLING FOOTAGE PROPOSED PHASE III MONITORING WELLS

WELL NO.		ESTIMATED TOTAL DEPTH (FT.)
MW-9		330
MW-10		375
MW-11		310
MW-12		215
MW-13		190
MW-14		415
	TOTAL	1,835

3.0 ISOTOPIC ANALYSES

3.1 Data

Samples were collected by Geochron Laboratories for ^{14}C, ^{13}C, ^{2}H, and ^{18}O analysis from six monitoring wells and the drilling water, and for ^{2}H and ^{18}O analysis from six surface waters, and for ^{18}O and ^{13}C analysis from rock chips near MW-4 and MW-8 (Table 2).

3.2 $\delta^{2}H$ and $\delta^{18}O$ Theoretical Considerations

Hydrogen has two stable isotopres, ^{1}H and ^{2}H, whose terrestrial isotopic abundances average 99.985% and 0.015%, respectively. (The superscript refers to the atomic mass of the isotope with respect to the atomic mass of the commonest carbon atom, carbon 12.) Water molecules therefore have nine different stable isotopic configurations whose atomic masses range from 19 to 22. Only the molecules $^{1}H_2{}^{16}O$, $^{1}H^{2}H^{16}O$, and $^{1}H_2{}^{18}O$, which represent 99.78%, 0.02%, and 0.20% of all water molecules, respectively, occur in amounts sufficient to be useful in hydrology.

The physio-chemical behaviors of these various isotopic forms of water depend on their chemical activities, which are related to their vapor pressures. The lightest water molecule, $^{1}H_2{}^{16}O$, has a significantly higher vapor pressure than does the heaviest molecule. The differences in chemical activities tend to concentrate water molecules containing the isotopes ^{2}H and ^{18}O in certain reservoirs (e.g. atmosphere, precipitation, ground water, surface water, ocean) in the hydrologic cycle by the process called isotope fractionation. Fractionation occurs during phase changes (e.g. solid to liquid, liquid to vapor, vapor to liquid). For example, the lighter and more volatile isotopic form $^{1}H_2{}^{16}O$ tends to evaporate preferentially

Table 2 Summary of Isotopic Analyses

Sample	δ^2H °/oo	$\delta^{18}O$ °/oo	$\delta^{13}C$ °/oo	^{14}C pmc
	Ground Water			
MW-2	-22	-3.8	-9.5	53.0 ± 1.3
MW-3	-19	-2.8	-5.1	10.1 ± 1.2
MW-4	-20	-3.0	-3.8	4.9 ± 0.6
MW-6	-16	-2.9	-5.9	21.6 ± 1.1
MW-7	-13	-2.2	-5.7	11.6 ± 1.0
MW-8	-12	-2.2	-12.0	13.0 ± 1.0
	Drilling Water			
	-5	-1.7	-9.5	119.1 ± 2.3
	Surface Water			
OF-1	-9	-1.8		
OF-2	-13	-2.3		
OF-3	-13	-2.0		
OF-4	-14	-1.7		
OF-5	-14	-1.8		
OF-6	-12	-1.8		
	Rock Chips at:			
MW-4		+30.0	-0.1	
MW-4		+29.6	-0.2	
MW-8		+29.4	-0.5	
MW-8		+29.5	+0.3	

to the heavier isotopic forms. Thus the vapor phase will be infinitesimally enriched in ^{1}H and ^{16}O, and the parent residual phase will be enriched in ^{2}H and ^{18}O. Conversely, precipitation is preferentially enriched in ^{2}H and ^{18}O with respect to the vapor phase which remains in the atmosphere.

Isotopic enrichment can be defined in terms of an equilibrium fractionation factor α. For example, in the isotopic equilibrium

$$({}^{1}H_2{}^{16}O + {}^{1}H_2{}^{18}O)_{\text{liquid}} = ({}^{1}H_2{}^{16}O + {}^{1}H_2{}^{18}O)_{\text{vapor}}$$

the fractionation factor $\alpha^{18}O$ is defined as:

$$\alpha^{18}O = \frac{R \text{ liquid phase}}{R \text{ solid phase}}$$

where R is the abundance ratio of the heavy/light nuclide.

The determination of absolute isotopic concentrations in a sample of water is extremely difficult. In hydrology it is conventional, and just as useful, to determine the relative isotopic composition of a sample with respect to a standard of known composition. Concentrations are therefore not expressed as absolute abundance ratios, R, but rather as relative δ units defined as:

$$\delta = \left(\frac{R \text{ sample}}{R \text{ standard}} - 1\right) \times 10^3$$

The δ unit expresses the differences in isotopic composition in parts per thousand (mil) between the sample and the standard. The standard for both ^{2}H and ^{18}O is Standard Mean Ocean Water (SMOW) defined by Craig (1961a). A sample having a $\delta^{18}O$ of -5 $^{o}/oo$ vs SMOW contains 5 parts per thousand less ^{18}O than does the standard. These isotopic differences are readily measured by dual trace mass spectrometry.

The ^{2}H and ^{18}O of precipitation generally obeys the relationship

$$\delta\,^{2}H = 8\,\delta\,^{18}O + d\ (^{o}/oo)$$

where d is the deuterium (^{2}H) excess. Craig (1961b) has shown this relationship to be

$$\delta\,^{2}H = 8\,\delta\,^{18}O + 10\ (^{o}/oo)$$

from analysis of over 1,000 samples of continental precipitation. This relationship is represented as line AB (Figure 4) and is known as the "Meteoric Water Line." Low latitude precipitations are generally isotopically heavier than high latitude precipitations. Meteoric water which has been subjected to excessive evaporation tends to plot on a line such as CD, whose slope is typically in the range of 4 to 6. Point C represents the isotopic composition prior to evaporation.

The isotopic composition of ground water may also be altered by interaction with aquifer minerals. At low temperatures (below 50 - 100°C), the kinetics of isotopic equilibrium are too slow to show any appreciable shift in composition, even when the water is exposed to the aquifer materials for very long times. At high aquifer temperatures, an isotopic exchange (exchange of isotopes between the water and the aquifer skeleton without a change in solute concentration) takes place. Because rocks generally contain little or no hydrogen, it is only the oxygen isotopic composition which alters. This exchange with the heavy isotopic reservoir (generally silicates in the aquifer skeleton) causes a translation in composition parallel to the $\delta\,^{18}O$ axis. A typical trend of thermal ground waters is shown as line EF in Figure 4, where point E represents the original isotopic composition.

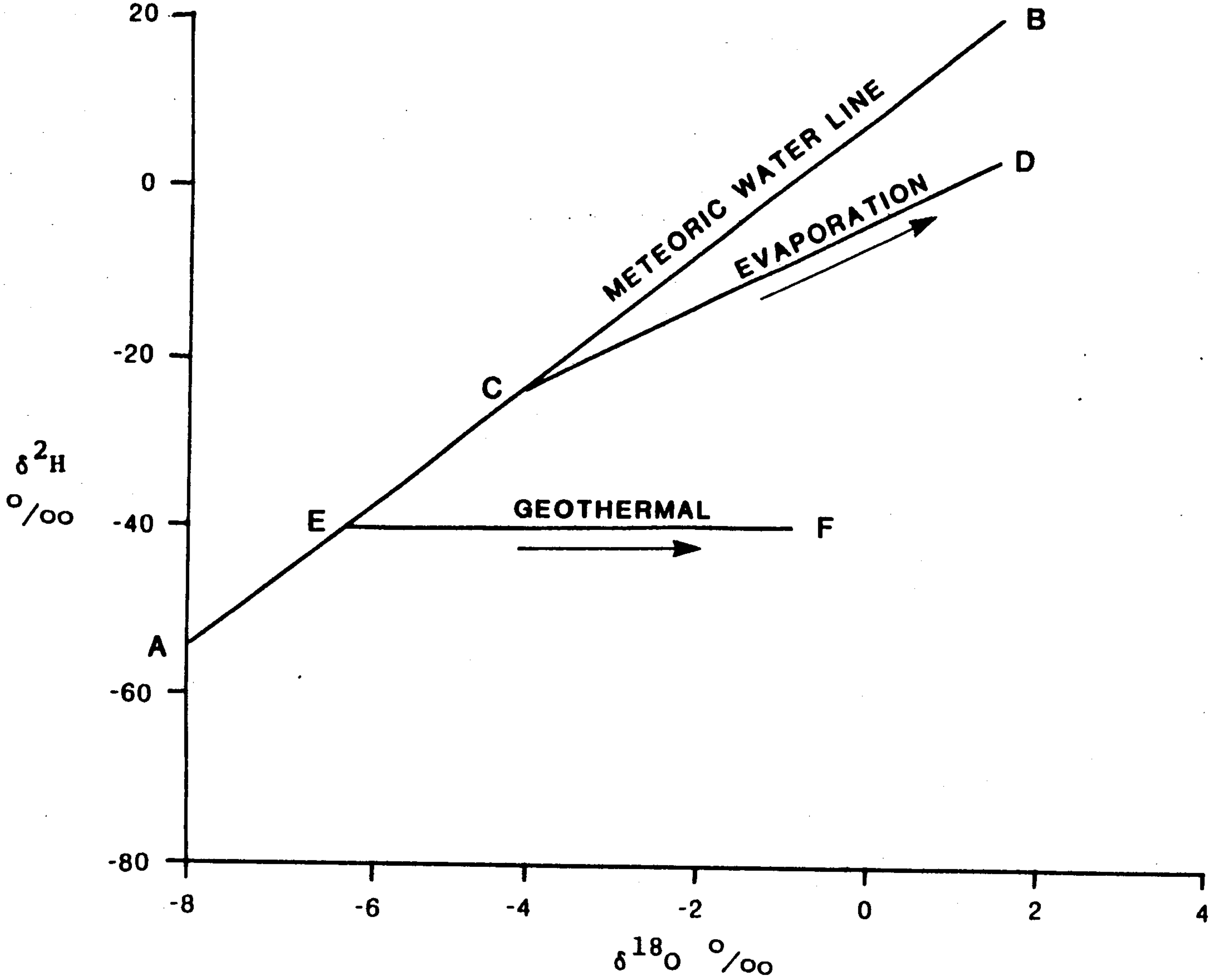


Figure 4 Schematic δ^2H and $\delta^{18}O$ plot. Line AB is the average global meteoric water line, line CD is a typical evaporation line, and line EF illustrates the variation in isotopic composition of hot water in a geothermal system.

Because isotopic fractionation is temperature dependent, the δ^2H and $\delta^{18}O$ of ground waters are often useful for evaluation of the origin of ground water, amount of rainfall, paleoclimate, seasonal recharge, sea water vs fresh water, subsurface thermal conditions and other factors affecting ground water.

3.3 δ^2H and $\delta^{18}O$ Analysis

The meteoric water line, defined as $\delta^2H = 8\delta^{18}O + 10$ (Craig, 1961b), is often used as a reference when, as in this investigation, local precipitation isotopic data are not available. All of the analyses from Table 2 and Figure 5 fall into the narrow range of -7 to -3.8 $^o/oo$ for $\delta^{18}O$ and -22 to -5 $^o/oo$ for δ^2H vs SMOW. (Note that only a small segment of the meteoric water line is shown on Figure 5.) None of the waters have undergone any process which has moved their stable isotope compositions appreciably away from the meteoric water line. Proximity of monitoring well water analyses to the meteoric water line indicates the Juana Diaz Formation waters are of meteoric, not saline connate, origins.

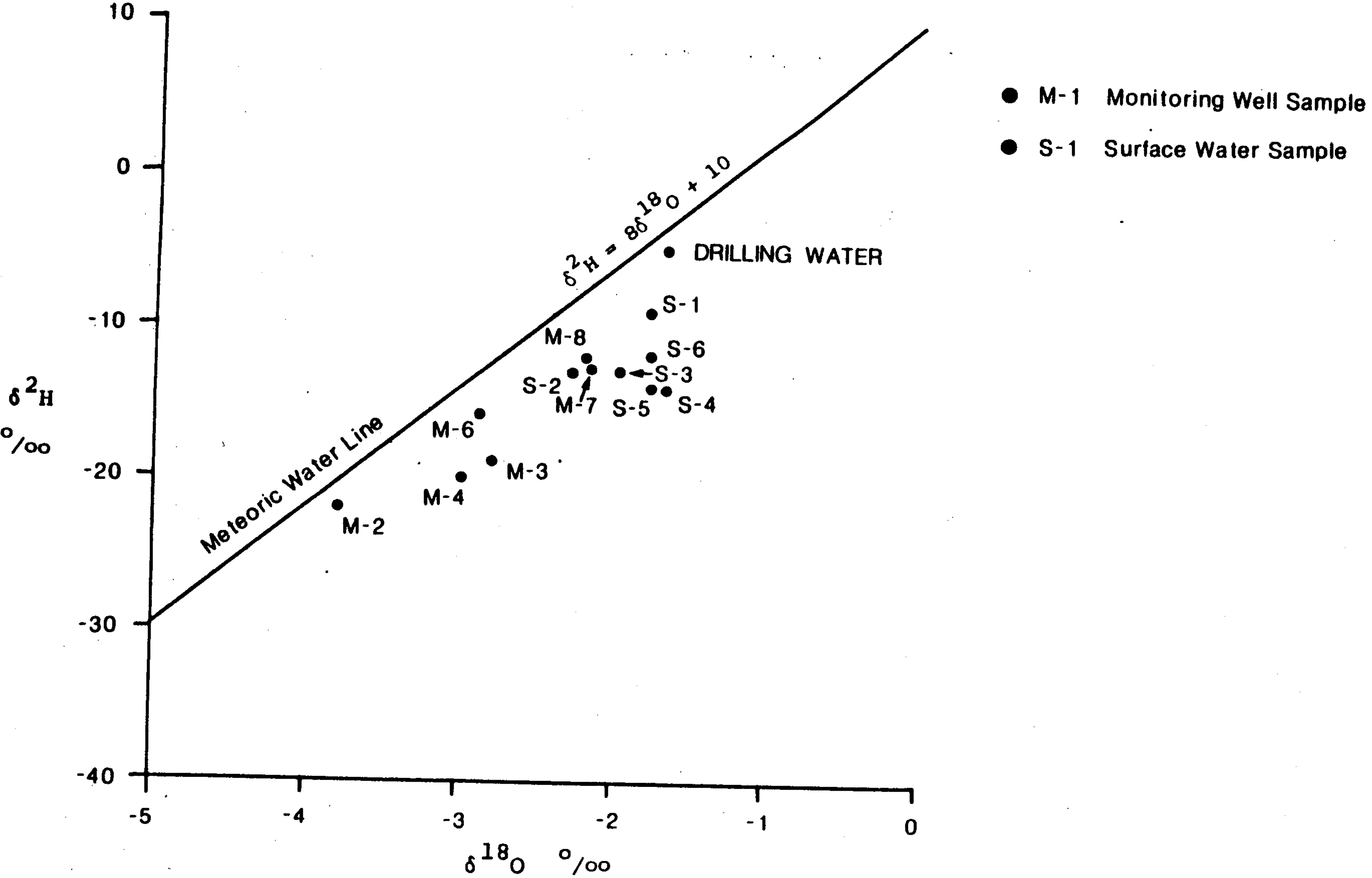
The isotopically light Juana Diaz Formation waters with respect to the isotopically heavier surface waters may indicate slightly cooler, about 1°C, and perhaps wetter paleoclimatic conditions during the recharge period of the Juana Diaz aquifer. Cooler conditions are suggested by the emperical global temperature relationships

$$\delta^2H = 5.6t - 100 \ ^o/oo, \text{ and}$$

$$\delta^{18}O = 0.695t - 13.6 \ ^o/oo$$

where t is the mean annual air temperature (Dansgaard, 1964) and the mean $\delta^{18}O$ and δ^2H values of surface waters are -1.9 and -12.5 $^o/oo$ respectively, and Juana Diaz Formation waters are -2.8 and -17.0 $^o/oo$ respectively. Recharge elevation variations and seasonal recharge effects, which may also be indi-

Figure 5 Plot of δ^2H and $\delta^{18}O$ analyses of gound water from the Juana Diaz Formation and offsite surface water. Standard meteoric water line is used for reference.



cated by the temperature relationships, are unlikely to be responsible for the observed differences in mean isotope values of the surface and Juana Diaz Formation waters.

The isotopically heavy drilling water, $\delta^{18}O$ of -1.7 and $\delta\ ^{2}H$ of -5.0 $^{o}/oo$, which was collected from the city water supply of Ponce, may be: 1) the result of evaporation fractionation during surface storage, or 2) representative of Ponce Formation water.

3.4 Radiocarbon Dating Theoretical Considerations

The concept ground-water "age" is confusing to some. A volume of water in an aquifer is the product of the admixture of many waters of possibly diverse origins and histories. The water has no unique age. When differences between the chemical behavior of dissolved carbonates and the water have been accounted for, the ^{14}C in solution can give an idea of the integrated mean subsurface residence time of the water.

The principles behind radiocarbon dating are best illustrated by the example of dating vegetal material. Radiocarbon is produced in nature by neutrons coming from cosmic ray spallation reactions colliding with atmospheric nitrogen, resulting in the reaction

$$n + {}^{14}N \longrightarrow p + {}^{14}C \, .$$

where n is a neutron and p is a proton. With time, a steady state has been approached between ^{14}C production by this reaction and depletion of ^{14}C from the atmosphere due to radioactive decay according to the reaction

$${}^{14}C \longrightarrow {}^{14}N + \beta^{-}$$

where β is a beta particle, and by transfer to other reservoirs of carbon (such as the ocean). This steady state value has been arbitrarily defined as 100 pmc (percent modern carbon). (100 pmc is defined to correspond to 13.56 decays per minute per gram of carbon.) Some fluctuations about this value have occurred due to variations in cosmic ray flux, but are negligible for most cases of dating. The burning of fossil fuels has diluted the atmospheric ^{14}C by the introduction of radiocarbon-free CO_2 since the Industrial Revolution, cauing the atmospheric concentration to descend below 100 pmc. Athrogenic radiocarbon has been injected into the atmosphere by thermonuclear bomb tests during the early 1960's, resulting in a northern hemisphere atmospheric peak of about 200 pmc. Transfer to the oceanic reservoir has reduced this value until presently it is about 130 pmc. These perturbations have occurred only since about 1880 and need be considered only when dating young materials.

Plants obtain all of their carbon from atmospheric CO_2. Therefore, except for a minor enrichment due to fractionation on the order of 2 pmc, the ^{14}C content of a living plant tissue is identical to that of the atmosphere. When this tissue dies, it is no longer resupplied with ^{14}C and radioactive decay slowly reduces the amount of ^{14}C in the plant at the rate of about half in 5,730 years. If the ^{14}C content of the plant material A_t is measured some time later as, say 25 pmc (i.e. 3.337 decays per minute per gram of carbon), the radioactive decay equation

$$t = \frac{5730}{\ln 2} \left(\ln \frac{A_t}{A_o}\right)$$

may be used to calculate the time (t) it has taken to reduce the initial activity (A_o) to the measured level (A_t). In the case of radiocarbon, whose half life is 5,730 years, to would be 11,560 years (because two complete half lives have elapsed to reduce this activity from 100 pmc to 25 pmc). Thus to date a sample, not only its current ^{14}C activity (A_t) must be known, but its initial ^{14}C activity (A_o) must be known or estimated.

Radiocarbon dating of ground water is not as straightforward as dating of of plant material. Recall tnat plant material has an A_o of 100 pmc and that the measured A_t is less than A_o only because of radioactive decay. There are two principal reasons why the A_t of ground water is not equal to atmospheric ^{14}C activity of 100 pmc. First, as with dead plant tissue, some ^{14}C has undergone radioactive decay. Second, ground water has acquired much of its carbon from sources having a ^{14}C activity of less than 100 pmc; therefore the A_o of the ground water is not equal to 100 pmc. The crux of dating ground water is estimating the initial ^{14}C activity (A_o) of the water at the time it became hydraulically isolated from the atmosphere.

Ground water may acquire carbon from several sources. These sources are illustrated in Figure 6 and are briefly discussed below (typical ^{14}C concentrations are for ground waters older than 200 years):

1) atmosphere (^{14}C = 100 pmc); only a small fraction of carbon found in ground water is of atmospheric origin because of the low atmospheric CO_2 partial pressure ($10^{-3.5}$ atmospheres).
2) biogenic production of CO_2 in the soil zone (^{14}C = 100 pmc); soil zone CO_2 has the same ^{14}C activity as the atmosphere because it comes mainly from root respiration of plants. The contribution of carbon from soil zone gas may be large because the CO_2 partial pressure may be as great as 10^{-2} to $10^{-1.5}$ atmospheres.
3) dissolution of carbonate minerals in the soil zone (^{14}C = 0 pmc);

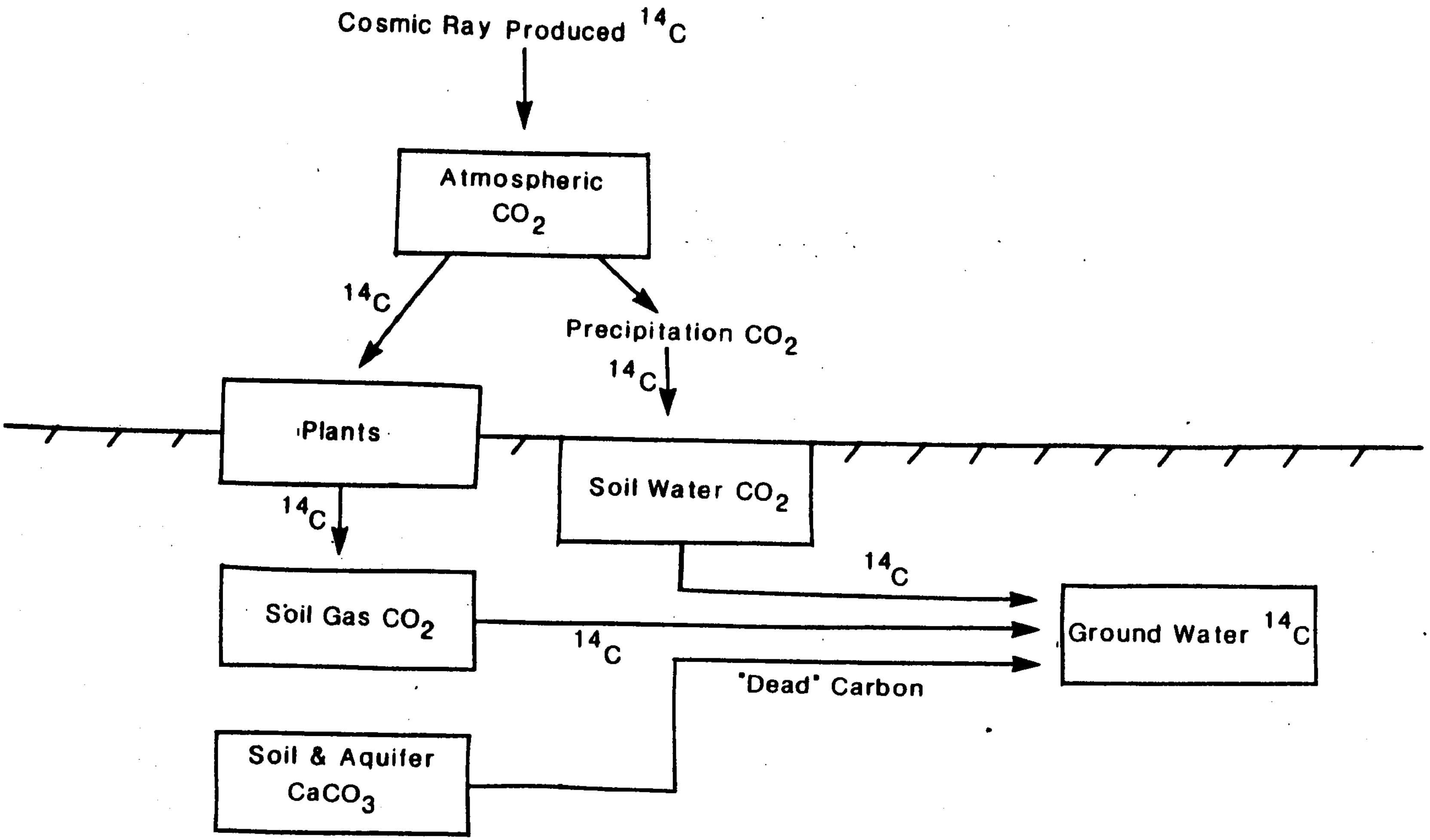

Cosmic Ray Produced ^{14}C
Atmospheric CO_2
^{14}C
Precipitation CO_2
^{14}C
Plants
^{14}C
Soil Water CO_2
^{14}C
Soil Gas CO_2
^{14}C
Ground Water ^{14}C
'Dead' Carbon
Soil & Aquifer $CaCO_3$

Figure 6 Schematic diagram illustrating the processes involving ^{14}C and their interrelations between the atmosphere, biosphere and upper lithosphere. Ground water acquires both carbon-14 and "dead" carbon.

soil zone carbonate minerals are generally considered "dead" because the carbon has existed long enough for any ^{14}C to decay completely. Most carbonate minerals in the soil zone are derived from bedrock minerals.

4) dissolution of carbonate minerals in the unsaturated zone and aquifer skeleton ($^{14}C = 0$); this carbon is also considered "dead" because it has existed long enough for any ^{14}C to decay completely.

5) in addition, isotopic fractionation and isotopic exchange processes can affect the ^{14}C activity and thus change the A_o.

A number of models have been developed for estimating the inital ^{14}C activity (A_o) of ground water. These models are based on 1) carbonate stoichiometry, 2) carbonate equilibrium, 3) isotope mixing, 4) isotope fractionation, and 5) combinations. These models are summarized by Fontes and Garnier (1979), Mook (1980), and Fontes(1983).

Only the Pearson (Pearson and Hanshaw, 1970) isotope mixing model could be used in this investigation because the data sets did not have field measured HCO_3^- concentrations which are required for the other models. The Pearson model is based on the fact that ^{14}C and ^{13}C behave chemically and isotopically identically, except that 1) ^{14}C is subject to radioactive decay and 2) a factor of 0.2 relates their fractionation factors. Thus ^{13}C can be treated as analogous to a non-decaying ^{14}C, and the initial ^{14}C activity (A_o) can thus be estimated. ^{13}C is a stable isotope and is also expressed in δ units ($\delta^{13}C$ is a measure of the ratio $^{13}C/^{12}C$ sample vs $^{13}C/^{12}C$ standard) as are ^{2}H and ^{18}O. The accepted standard for ^{13}C is a sample of Belemitella americana from the Pee Dee Formation (PDB) in South Carolina.

The Pearson isotope mixing model is illustrated in Figure 7. The ^{14}C

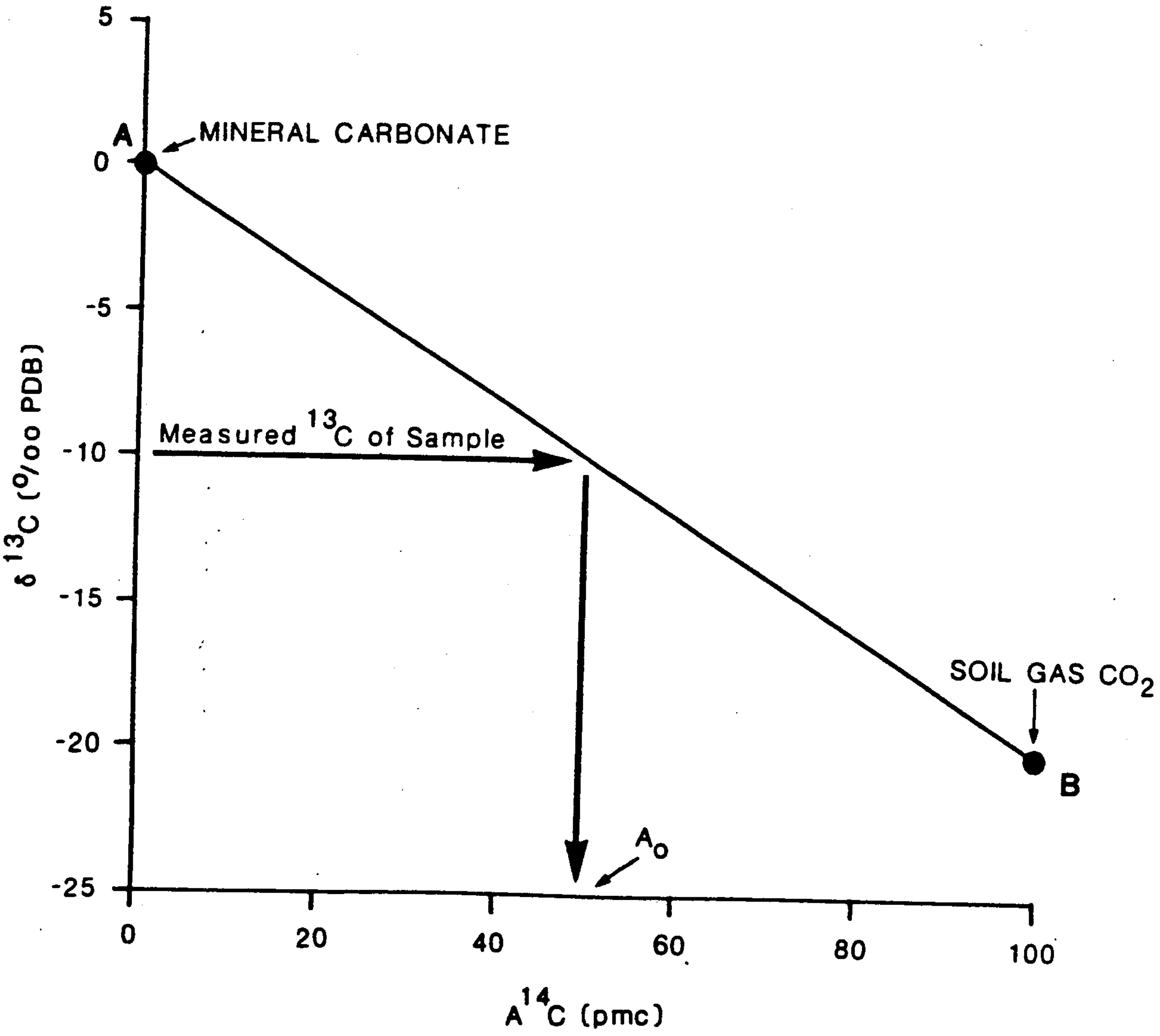


Figure 7 Schematic diagram illustrating the linear isotope mixing model (Pearson model) for estimating initial carbon-14 activity (A_o) of the ground-water sample. See text for discussion.

activity of the carbonate mineral phase is plotted at zero pmc, while the ^{13}C content is shown as 0 °/oo vs PDB. The vast majority of continental mineral carbonates fall within this range. The ^{13}C content of mineral carbonate samples from the study area has been determined. The initial ^{14}C activity of the soil gas is considered to be 100 pmc and the ^{13}C content of this gas approached the ^{13}C composition of vegetative cover of the area. Typical soil gas ^{13}C values for climates are (Fontes and Garnier, 1979):

Climate	$\delta^{13}C$ (PDB) °/oo
temperate	-25
intermediate	-20
tropical	-12

Because the $\delta^{13}C$ of each group of plants may vary several per mil from the climatic average and the vegetal cover of an area may have changed since recharge occurred, the $\delta^{13}C$ of the soil gas must be estimated. The $\delta^{13}C$ of the soil gas CO_2 has been set at -20 °/oo in the example in Figure 7. Because the carbon in ground water was acquired from both soil gas CO_2 and carbonate minerals, the A_o and initial $\delta^{13}C$ of the ground water must lie somewhere along the mixing line between the two end members labeled A and B. If a value of -10 °/oo is determined, and it is assumed that it represents both the initial and the final ^{13}C content of the water (since it does not undergo decay), then the initial ^{14}C content may be projected as 50 pmc. The estimated A_o is then used with the measured activity of the water sample (A_t) to estimate the ground water age by means of the law of radioactive decay.

Rather than graphically solving for A_o, the following equation, based on similar triangles, is used:

$$A_o = \frac{\delta_t - \delta_c}{\delta_g - \delta_c} (A_g - A_c) + A_c$$

3.5 ^{14}C Estimated Ground-Water Ages

Mean subsurface residence times ("ages") have been estimated for 6 ground-water samples and the drilling water. Four sets of age estimates were calculated (Table 3). The first estimate, "Raw Age," is unadjusted for "dead" carbon contributions and is the age if the sample were of organic origin. The Raw Ages are therefore older than the maximum possible mean residence times of the ground waters.

Two sets of age estimates, Age 1 and Age 2, were made using the Pearson isotope mixing model (Pearson and Hanshaw, 1970). These estimates assume:

1) a ^{14}C activity of the soil gas CO_2 (A_g) of 100 pmc,

2) a ^{14}C activity of the mineral carbonate (A_c) of 0 pmc,

3) a δ^{13}C of the mineral carbonate (δ_c) of 0.1 $^o/oo$ (based on analysis of carbonate rock chips at MW-4 and MW-8, Table 2 , and

4) a δ^{13}C of the water samples (δ_t) as measured (Table 2).

Soil gas $CO_2\delta^{13}$C data are not available from the study area. The δ^2H and δ^{18}O data, previously presented, suggest the climate at the time of recharge was not greatly different than present conditions (approximately 1°C cooler at the time of recharge). Based on present climatic conditions the δ^{13}C of the soil gas is estimated to be in the range of -22 to -18 $^o/oo$ vs PDB; Age 1 and Age 2 estimates are based on these values, respectively.

The δ^{13}C values of the ground-water samples (Table 2) are not typical either of waters circulating in inorganic marine carbonates or of organic sediments. Marine carbonates have δ^{13}C values of +4 to -4 $^o/oo$ (Craig, 1963; Truesdell and Hulston, 1980; and Giggenbach and others, 1983). The intermediate δ^{13}C values of the ground-water samples suggest the ground waters have undergone: 1) isotopic fractionation (^{13}C - ^{12}C) in the unsaturated zone of

Table 3 Estimates of Mean Ground-Water Residence Times

Sample	A_t ^{14}C pmc	Raw Age years	Age 1 A_o (δ_g -22 $^o/oo$)	Age 1 years	Age 2 A_o (δ_g -18 $^o/oo$)	Age 2 years	Age 3 A_ρ (δ_g -22, ε -9 $^o/oo$)	Age 3 years
MW-2	53.0	5,250 ± 200	40.6	nc[1]	49.7	nc	68.5	2.100 ± 200
MW-3	10.1	18,950 ± 900	22.8	6,700 ± 950	27.9	8,400 ± 900	38.5	11,000 ± 850
MW-4	4.9	24,000 ± 1000	16.9	10,200 ± 1000	20.7	11,900 ± 950	28.5	14,500 ± 900
MW-6	21.6	12,700 ± 400	26.5	1,700 ± 400	32.4	3,350 ± 400	44.6	6,000 ± 400
MW-7	11.6	17,800 ± 650	25.6	6,500 ± 650	31.3	8,200 ± 650	43.1	10,800 ± 600
MW-8	13.0	16,400 ± 600	20.5	3,800 ± 650	25.1	5,400 ± 650	34.9	8,200 ± 650
Drilling Water	119.1	modern						

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[1] nc = no age can be calculated because A_t is greater than A_o. The calculated age would be in the future.

the aquifer after attaining closed system conditions (confined), or 2) fractionation (^{13}C - ^{12}C) during sampling. The high SO_4^{2-} concentration of the samples may have resulted in some carbon not precipitating during sampling. This non-precipitated portion may then have fractionated with the precipitated portion. In any event, the Pearson model is not appropriate for fractionated ground waters, as it will yield estimated ages which are too young. The extent of fractionation is not possible to determine without the use of a HCO_3^- based model.

The fourth estimate, Age 3, is based on an isotope mixing model modified for fractionation (Fontes, 1983). This model assumes complete HCO_3^- exchange with soil gas CO_2, which is not the case in the study area, because the modification is only valid for fractionation in the unsaturated zone, and it is more likely that fractionation may have occurred during sampling. The modeled results illustrate the effect of fractionation on modeled ages, and therefore Age 3 results are instructive. Age 3 estimates are not considered reliable fractionation-adjusted ages. The fractionation-adjusted model is

$$A_o = \frac{\delta_t - \delta_c}{\delta_g - \varepsilon_g - \delta_c} (A_g - A_c) + A_c$$

where all factors are the same as the Pearson model except ε_g is a fractionation factor, assigned a value of -9 ^{o}/oo based on the aquifer temperature.

Precise mean ground-water residence times cannot be estimated because only one model could be used, and there appears to have been isotopic fractionation. Age 1 estimates may be considered as representative of the minimum mean residence times.

4.0 OBSERVATIONS ABOUT THE GROUND-WATER FLOW REGIME

The Ponce Waste Facility lies in the southern Carbonate Province which consists of the Oligocene-Miocene Juana Diaz Formation and the overlying Miocene Ponce Limestone. The Juana Diaz Formation generally has low ground-water transmitting properties and the Ponce Limestone has a greater hydraulic conductivity. Because of a regional southerly dip of the rocks in the Province, the Juana Diaz Formation tends to crop out in the northern portions of the Province and the younger Ponce Limestone tends to crop out to the south, an area which includes the project site.

A major east-west trending fault divides the project site in half; Ponce Limestone crops out north of the fault and the Juana Diaz Formation crops out in the southern half of the site. The uplifted block of Juana Diaz Formation extends to the east and west from the site for several kilometers. South of the project site the Juana Diaz Formation appears to dip under the Ponce Limestone. Several faults of small displacement have been identified in the Juana Diaz Formation on the project site (Law Engineering, 1983).

The focus of this report has been on the ionic and isotope geochemistry of ground-water samples from the Juana Diaz Formation taken from the project site. From these data and geologic and potentiometric data provided by Law Engineering some generalized observations may be made regarding the ground-water flow regime in the Juan Diaz Formation at the project site. These data do not allow an interpretation of regional ground-water flow regimes in the Ponce Limestone.

The ground-water flow regime in the Juana Diaz Formation at the project site is not typical of a high flow rate, fast flushing ground-water system.

The ground-water system is complex and does not appear to have good hydraulic conductivity between monitoring wells. Neither the geochemistry nor the potentiometric data allow the interpretation of exact ground-water flow patterns.

The δ^2H and $\delta^{18}O$ data suggest the ground waters are of meteoric origin and may have recharged during slightly cooler climatic conditions. The ground waters appear to have picked up their relatively high solute concentrations by contact with the Juana Diaz Formation. From the solute chemistry it is not possible to determine whether these ground waters circulated in the Ponce Limestone prior to entering the Juana Diaz Formation; however, it could be possible to determine whether Ponce Limestone waters have circulated in the Juana Diaz Formation on the basis of solute chemistry.

The wide variation in estimated mean ground-water residence times from such closely spaced wells in the same formation is unusual. Such variations could be accounted for by 1) sampling or laboratory analytical errors, 2) unaccounted isotopic fractionation or isotopic exchange, or 3) actual variations in mean residence times. There is no evidence to suggest laboratory analytical errors in the carbon analysis. Such errors are commonly systematic, and the wide variation in ages does not appear to be systematic. There is the possiblity that the variation may be, in part, due to the previously discussed fractionation resulting from incomplete precipitation of carbon in the sample bottle due to the high SO_4^{2-} concentrations of the water samples. The amount of incomplete precipitation could vary from sample to sample, thus producing an unsystematic variation in estimated ground-water ages.

Natural isotope fractionation and exchange processes, which have probably occurred, should have a minimal non-systematic effect on modeled radiocarbon ages. From the data available it appears reasonable to conclude that there is a several thousand year variation in mean residence times of ground waters in the Juana Diaz Formation at the project site and that the Age 1 estimates are the minimum mean times since these waters became hydraulically isolated from the atmosphere and soil gas CO_2.

There does not appear to be a correlation between geochemical, isotopic, potentiometric, and geologic data which would suggest specific ground-water flow patterns. The general absence of chemical and isotopic correlations may be illustrated by two examples. First, MW-2, for which mean residence time cannot be estimated because A_o is less than A_t, has a greater solute concentration than does MW-7, which has an estimated mean residence time of 6,500 years. Additionally, MW-2 is isotopically light, with a δ^2H of -22 $^o/oo$ and a $\delta^{18}O$ of -3.8 $^o/oo$, which suggests the young age of the water is not the result of dilution with isotopically heavy drilling water or surface water. Second, MW-3 and MW-7 have approximately the same estimated mean ground-water residence times, 6,500 and 6,700 years, respectively, yet have substantially different solute concentrations and have different stable isotope compositions. The δ^2H and $\delta^{18}O$ concentration of MW-7 is similar to surface water, whereas MW-3 has an isotopic concentration more typical of Juana Diaz Formation waters (Figure 5). MW-7 also has a very low solute concentration for a Juana Diaz ground water (Figure 2).

Correlations between potentiometric, hydrostratigraphic, and isotopic data are inconsistent. Monitoring wells MW-4 and 6, and wells MW-4 and 3 offer an opportunity to examine these relationships in an area where faults between the wells are not known to exist. (Faults may act as hydraulic barriers or flow conduits, thus affecting potentiometric data.) MW-4 and MW-6 lie approximately along the strike of the Juana Diaz Formation, and MW-4 and MW-3 lie approximately strike normal or parallel to the dip of the formation. Thus equal elevations in boreholes MW-4 and MW-6 should sample the same hydrostratigraphic horizon (aquifer), and the same elevations in boreholes MW-4 and MW-3 should sample a lower stratigraphic horizon in MW-4 than in MW-3. Potentiometric levels of 181.3 and 186.3 feet in MW-3 and MW-4, respectively, suggest ground water in overlying younger beds would tend to move to the underlying older strata. In other words, ground water would move from the surface downward toward the deeper regions of the formation. The mean residence times of 6,700 and 10,200 years for MW-3 and MW-4 support this conclusion. The differences in mean residence time could be partially accounted for by the very low hydraulic conductivities, 10^{-8} to 10^{-9} cm/sec, of the non-water-producing horizons (Law Engineering, 1983).

Monitor wells MW-4 and MW-6 have a similar potentiometric relationship; lower and deeper water-bearing horizons in MW-6 have lower potentiometric levels than the higher horizons in MW-4, suggesting downward movement of ground water. Mean ground-water residence times, however, suggest an upward movement of ground water. Ground water from the deeper stratigraphic horizon in MW-6 has a mean residence time of 1,700 years, whereas the younger horizon in MW-4 has a mean residence time of 10,200 years.

Additionally, the ground water encountered in the 172 foot bed in MW-4 was not encountered in the same bed at MW-6, even though the bed was encountered at MW-6 at the 172 foot elevation. The non-continuity of ground water in this bed suggests: 1) a fault may exist between the two monitoring wells; or 2) the fine grained sediments of the Juan Diaz Formation do not have lateral homogenity, and thus aquifers are not laterally continuous along a stratigraphic horizon. Non-lateral continuity of aquifers, whose hydraulic conductivities are 10^{-4} to 10^{-6} cm/sec (law Engineering, 1983), would result in pockets of ground water separated by materials of lower hydraulic conductivities. Such aquifers could have steep hydraulic gradients between them, as the potentiometric data suggest, and thus the transfer of ground water from one water-bearing zone to another would be slow.

Correlation of potentiometric data and geochemical data from opposite sides of the small displacement faults mapped on the sites is not possible. The amount of stratigraphic offset along these faults is unknown, and to date geophysical and well log correlations across the faults have been unsuccessful. The physical relationships between aquifers and hydrostratigraphic units across the faults are therefore unclear.

Large potentiometric differences and variations in estimated mean ground-water residence times across the faults suggest slow ground-water movement from one fault block to another. The faults may not have an effect on ground-water flow, or they may act as a hydraulic barrier promoting the observed differences in potentiometric levels and ground-water ages. If the faults were hydraulic conduits, potentiometric levels and ground-water residence times would tend to equalize on opposite sides of the faults. If the faults are hydraulic barriers, each fault-bounded block of strata could have a ground-water flow system with a limited hydraulic connection with adjacent fault-bounded flow systems. In this case, ground-water flow patterns (vertical and horizontal) and the relationship between potentiometric levels and mean ground-water residence times could vary from block to block. Similar relationships could, however, occur if the faults are neutral with respect to ground-water flow and the water-bearing zones are pockets separated by very low hydraulic conductivity material.

5.0 DATA LIMITATIONS

Chemical analyses of ground-water samples from 6 onsite and 4 offsite wells were reviewed. Many of the wells had analyses from several sampling dates. Cation-anion imbalances as great as 30% were found in several of the data sets. Because ground water is electrically neutral, such imbalances suggest sampling or analytical errors. Data with imbalances greater than 5% generally are not considered sufficiently reliable for use in aquifer analyses. Additionally, most of the data sets did not have HCO_3^- results. (HCO_3^- is the dominant species at the field pH.) HCO_3^- is a major anion and is required for chemical evaluation and most radiocarbon modeling techniques. Estimates of HCO_3^- were obtained from offsite data and the most recent alkalinity test for onsite wells (Gustin, 1984). The estimated HCO_3^- concentrations may be used in this investigation for a general review of the water chemistries because these concentrations are small relative to the other anions present. These estimates may not be used in radiocarbon modeling.

6.0 CONCLUSIONS

1) Ground water in the Juana Diaz Formation under the project site is of meteoric (rain) origin.
2) Ground waters may have recharged under cooler (about 1°C) paleoclimatic conditions.
3) Existing surface waters near the site do not appear (on the basis of ^{2}H and ^{18}O analyses) to be the origin of the ground water sampled in the monitoring wells.
4) Ground waters in the Juana Diaz Formation under the site have different solute chemistries than do Ponce Limestone ground waters, and they may be distinguished from them.
5) Mean subsurface residence times of ground water in the Juana Diaz Formation under the site appear to be thousands of years.
6) The ground-water chemistry, isotope data, and geologic and potentiometric data from the project site suggest that ground-water flow in the Juana Diaz Formation at the site is not part of an active, fast flushing, well hydraulically connected ground-water flow system.

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